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(54) Title of Invention

Ceramic Carrier for Bioreactor

(57) Abstract

Purpose

To enable production of a ceramic carrier having an organic thin film for fixing a microorganism or enzyme stably for a long time to a ceramic honeycomb carrier or porous ceramic carrier that is used in chemical reactions.

Constitution

Instead of a conventional ceramic carrier with a smooth surface, it is a ceramic carrier obtained by modifying the surface of a bead, pellet, or horseshoe-shaped ceramic carrier to needle or prismatic mullite crystals that are 1-100 μm long and 0.1-10 μm thick in a highly dense, turf-like state and then embedding a cross-linked chitosan film between the mullite crystals.

Effects

Because the surface of the ceramic carrier is constituted by mullite crystals in a turf-like state, a chitosan film is easily bonded to the ceramic carrier with strong adhesion in order to support an enzyme or microorganism stably for a long time, and biocatalyst activity can be sustained over a long period of time.

CLAIMS

1. A ceramic carrier with a chitosan film obtained by immersing a ceramic carrier in an acetic acid solution that contains chitosan whose molecular weight has been lowered with hydrogen peroxide, then fixing the chitosan with a potassium hydroxide solution, and subsequently crosslinking it with glutaraldehyde.

2. A bioreactor carrier that is stable for a long time, which is obtained by growing needle or prismatic mullite crystals that are 1-100 μm long and 0.1-10 μm thick in a highly dense turf-like state on the surface of a bead, pellet, or horseshoe-shaped ceramic carrier or a ceramic monolith having a honeycomb structure and then embedding a chitosan film between the crystals.

DETAILED DESCRIPTION OF THE INVENTION

[0001]

Industrial field of use

The present invention relates to a material for fixing a microorganism or enzyme stably for a long period of time to a ceramic honeycomb carrier or porous ceramic carrier used in chemical reactions.

[0002]

Prior art

Biochemical reactions that utilize enzymes or microorganisms are widely used in such fields as foods and medicines. The methods of fixing enzymes and microorganisms to the surface of ceramic carriers used in the past are the physical adsorption method, which adsorbed them directly on the carrier surface, the covalent bonding method, which covalently bonded an enzyme or microorganism to the surface of a water-insoluble bead or pellet carrier, and the crosslinking method, which crosslinked a microorganism to a carrier using a crosslinking agent such as glutaraldehyde or bisdiazobenzidine.

[0003]

Problems the invention is to solve

However, in the case of the physical adsorption method of the past, the enzyme was apt to peel from the carrier during the reaction because of weak adhesion between the carrier and enzyme, and high reaction activity could not be expected. And with the methods of covalent bonding and crosslinking, there was the problem that the microorganism was markedly modified or degraded by fixation, which led to a decline in activity of the reaction. Another problem of the covalent bonding method was that the amount of enzyme that could be fixed was limited.

[0004]

Means of solving the problems

The present invention is the development of a ceramic carrier with an organic thin film on the surface that strongly adheres to the ceramic carrier and is stable for a long time so that the enzyme or microorganism is not modified or degraded by the supporting treatment. This invention, instead of the conventional carrier having a smooth surface, is a carrier that has a porous texture structure obtained by modifying the surface of a ceramic carrier to needle or prismatic

mullite crystals having a length of 1-100 μm and thickness of 0.1-10 μm in a highly dense, turf-like state. This invention obtains a ceramic carrier that can support a thin film which is outstanding in the permeability of liquids and which bonds strongly to the surface.

[0005]

In this invention, a ceramic carrier is first immersed in an acetic acid solution that contains chitosan whose molecular weight has been lowered with hydrogen peroxide, and then that chitosan is fixed with a potassium hydroxide solution and subsequently crosslinked with glutaraldehyde to give a ceramic carrier with a chitosan film, so a carrier with outstanding adhesion of enzymes or microorganisms and also quantity thereof adhered is obtained.

[0006]

In the case of this invention, the surface of the ceramic carrier is innumerable fine mullite crystals in a turf-like state. Therefore, the chitosan thin film readily permeates between the individual mullite crystals, resulting in a structure where the chitosan thin film is embedded between the crystals, so an organic film that does not readily peel from the ceramic carrier can be obtained. In the case of conventional ceramic carriers, the surface of the carrier was smooth and permeability of the film into the carrier was extremely low, so the peel strength of the film declined.

[0007]

Practical Example 1

A porous alumina body having a porosity of 40% and pore diameter of 0.6 μm was immersed in a 1.0% acetic acid solution containing chitosan whose molecular weight was lowered to 10,000-20,000 with 0.03% hydrogen peroxide in a concentration up to 1.5% for 30 minutes while deaerating. Then it was fixed with a 5% potassium hydroxide solution, and a crosslinking reaction was also carried out with 5% aldehyde to support a chitosan film on the surface of the porous ceramic. By repeating these operations and increasing the number of times it is immersed in the chitosan solution, the thickness of the chitosan film can be varied from 10 μm to 1,000 μm. Moreover, by varying the chitosan solution in a range up to 10%, the film thickness can be increased to a maximum of 3 mm. The bonding strength of chitosan films from 10 to 100 μm thick supported on the porous alumina body was 6-8 kg/cm^2.

Practical Example 2

Clay mineral containing alumina and silica was molded into a honeycomb and dried, following which it was fired at 1,400-1,700°C to prepare a honeycomb ceramic. This honeycomb contained silica glass that was soluble in acid or alkali and mullite that was insoluble in acid or alkali, so when the surface layer was chemically etched with 2.3-9.2% hydrofluoric acid, needle or prismatic mullite crystals 1-100 μm long and 0.1-10 μm thick were exposed in a turf-like state on the surface. The texture constituted by the individual mullite crystals was a porous structure with innumerable pores 0.1-1.0 μm in diameter. The bonding strength of chitosan thin films approximately 10 to 100 μm thick that had been supported by the treatment of Practical Example 1 on ceramic carriers having this porous texture structure was 12-20 kg/cm^2. On the other hand, the bonding strength of chitosan thin films supported by the same chemical treatment on smooth ceramic carrier surfaces that had not been etched was 0.5-2.0 kg/cm^2.

Practical Example 3

Glucoamylase was fixed by adsorption to the surface of the honeycomb ceramic carrier covered with chitosan prepared in Practical Example 2. Batch and flow-through reaction experiments were carried out under conditions of a solution temperature of 50°C and pH 4.5 using starch (10/L) as substrate, and the concentration of the resulting glucose was determined by the enzyme method. First, in the batch reaction experiments using a fixated enzyme prepared by immersing carriers supporting different amounts of chitosan in enzyme solutions of the same concentration, the initial reaction rate increased almost linearly with increase in weight of chitosan, and the advantage of increasing the thickness of the film was confirmed. Also, in the flow-through reaction experiments in which the residence time of the reaction solution was varied in a range of 0.5-2 hours, a glucose conversion of 50-95% could be attained. The reactor activity could be increased by five-fold or more by increasing the concentration of the enzyme solution used at the time of fixation. Also, the half-life of reactor activity in flow-through reactions was approximately three days in the case of unmodified chitosan because the enzyme gradually peeled off. But by introducing a tertiary amine or quaternary amine into this, half-life was drastically improved and the activity was so stable that half-life could not be estimated. Moreover, the chitosan film did not peel even with continuous use for more than a month, and the effect of stabilizing by embedding part of the chitosan film in the needle mullite crystals on the surface of the ceramic support was confirmed.